

Progress in Negative Tone Organic Resists Based on Epoxide Cross-linking for EUVL

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Ultraviolet Lithography

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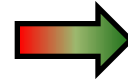


1. Why negative tone cross-linking molecular resists?
2. General performance/capabilities
3. Controlling cross-linking in these systems
4. EUVL results
5. Future work



Fundamental Problems for High Resolution Resists

-Utilization of molecules and imaging schemes that possess a small “pixel” size



Molecular resist platforms

-Ability to resist pattern collapse



Cross-linked organic materials as final features

-Ability to tailor amplification level and build in amplification to improve LER and resolution



Utilization of photo-responsive quenchers

-A design that can prevent resist inhomogeneity

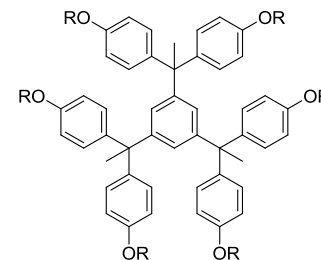
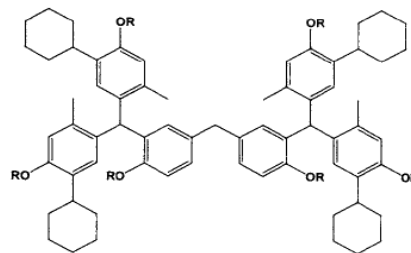
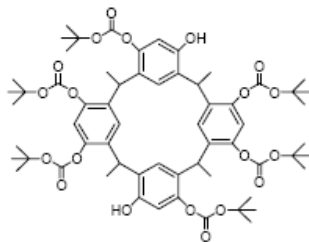
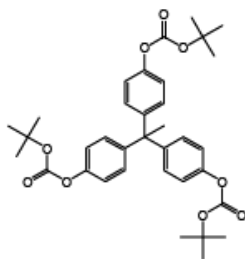


Small molecule resists

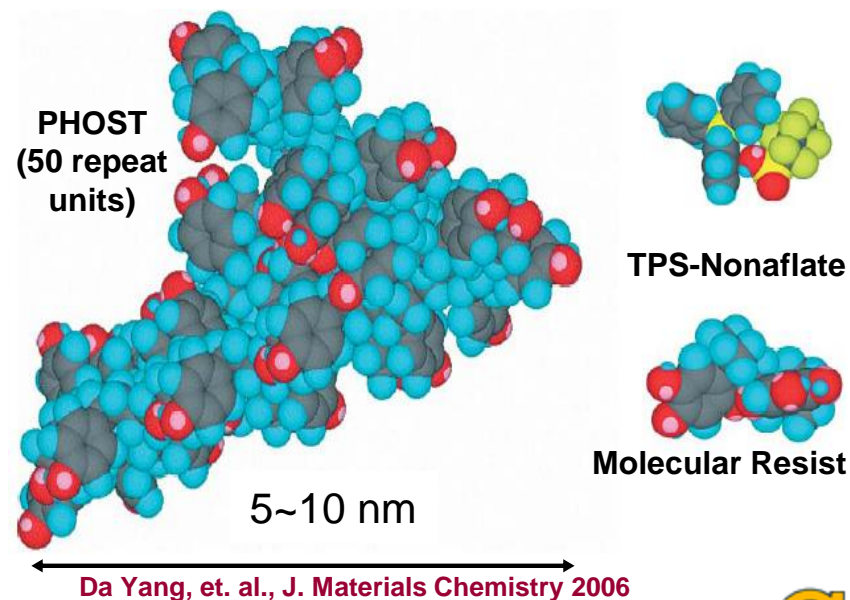


Molecular Resists

- Molecular glasses are low molecular-weight organic compounds that readily form stable amorphous glasses

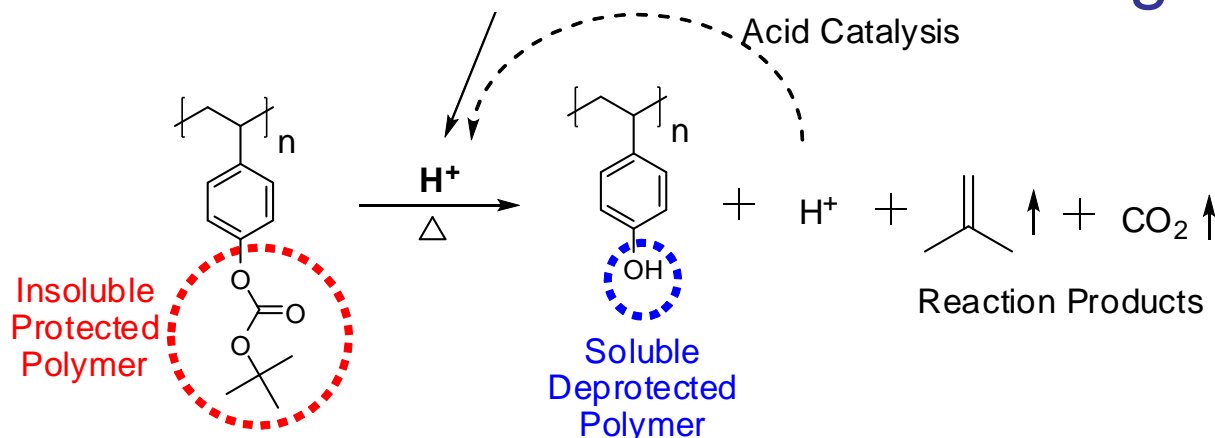


- Introduced to improve resolution but had other issues for positive tone
- Use for negative tone cross-linked resists appears much more favorable
- Good properties include:
monodisperse & synthetic control

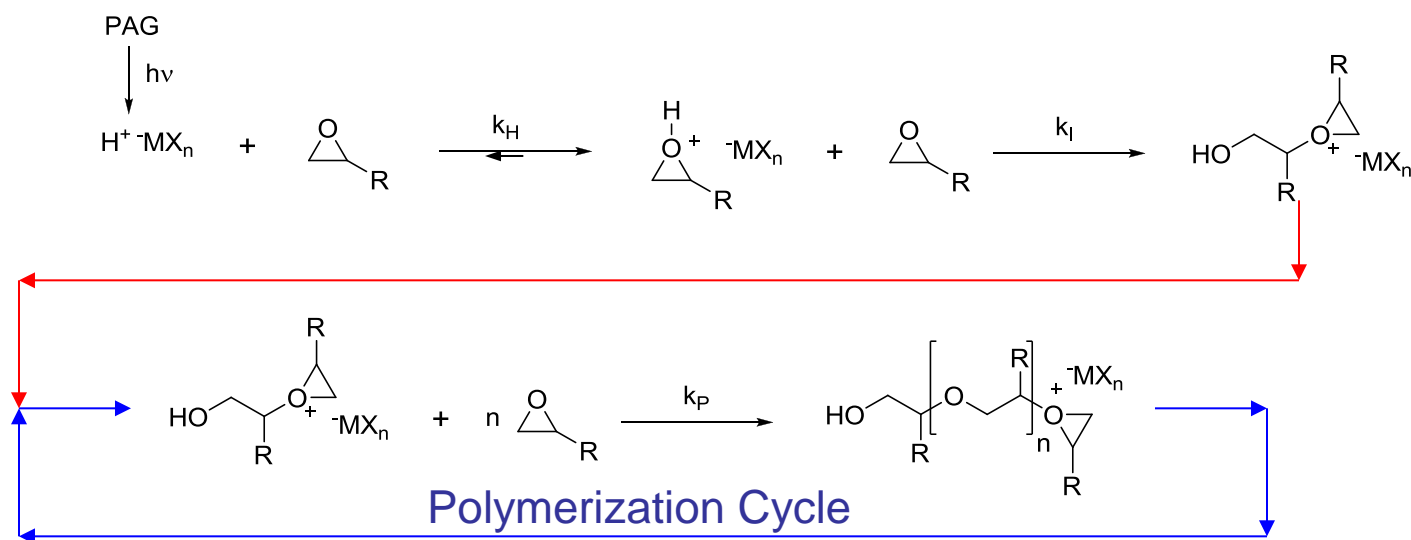


Neg. Tone MR with Cationic Cross-linking

Positive Tone



Negative Tone

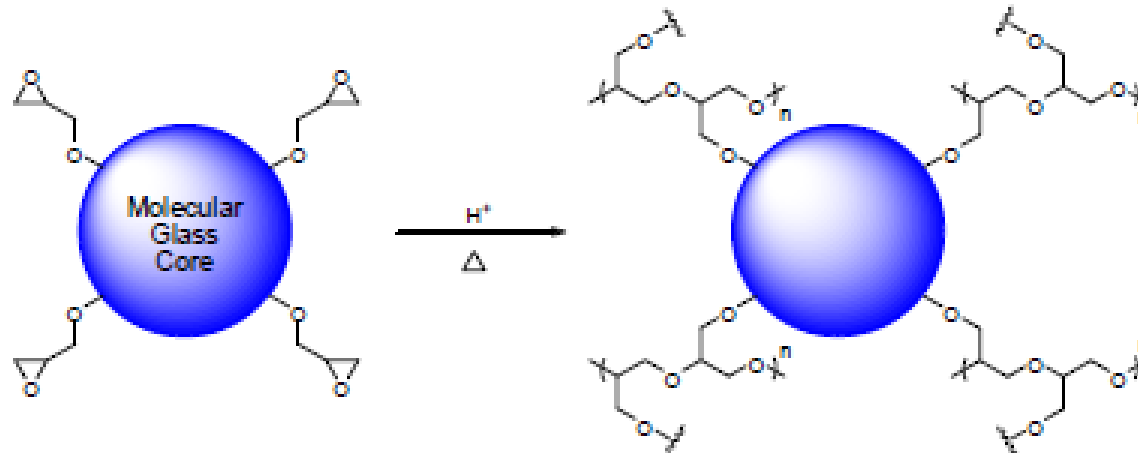


- There are mechanistic changes in the patterning that affect performance
- Photoacid is no longer the most important reaction species – active cation instead – the cross-linking must be controlled, not the acid



Neg. Tone MR with Cationic Polymerization

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Potential advantages of cationic polymerization MRs

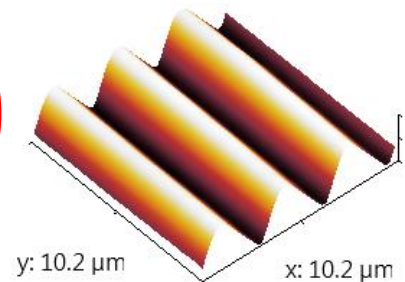
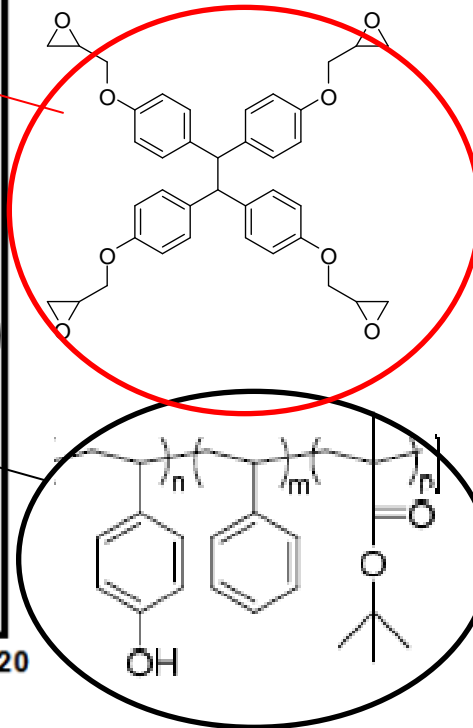
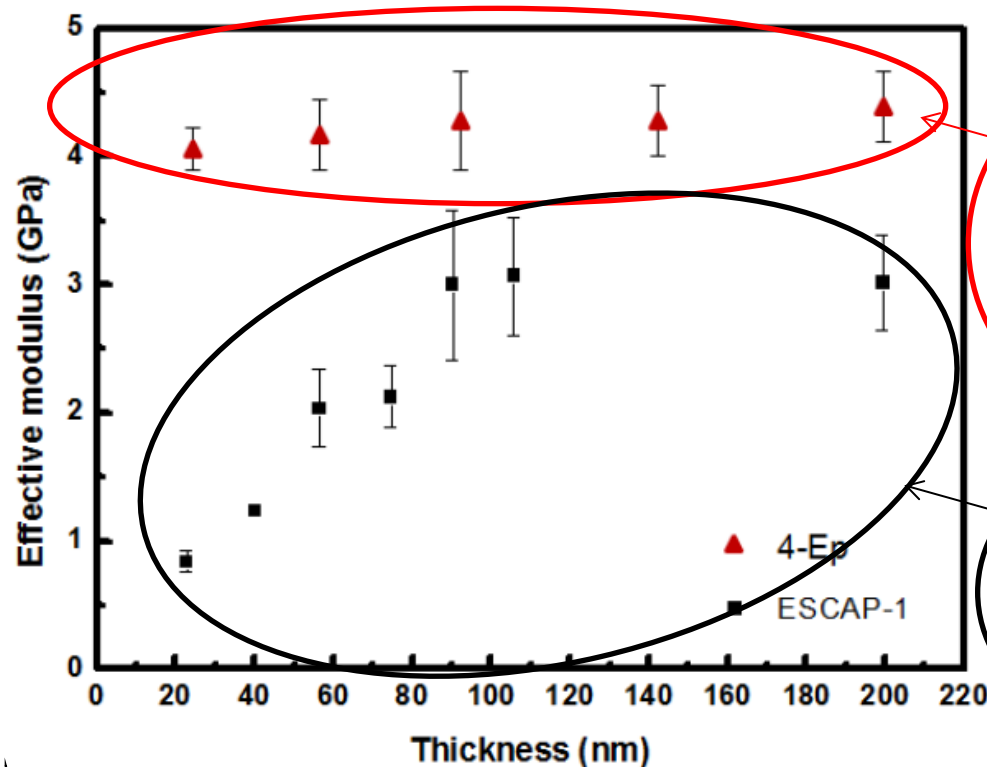
- superior mechanical strength
 - cross-linking increases modulus, improves pattern collapse
- intrinsic diffusion control
 - active cation is covalently attached to end of growing chain/network
 - diffusivity decreases with extent of conversion
- low outgassing of resist
 - no mass loss during reaction vs. deprotection schemes
- reduced swelling vs. polymers
 - higher cross-link density in MR reduces swelling



Improved Mechanical Properties of Cross-linked Resists

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- Using thin film bucking method, we can measure the modulus for ultra-thin films (SPIE 76391I, 2010)
- Cross-linked MR show higher modulus than positive tone polymeric resists both in bulk and ultra-thin films
- This leads to improved pattern collapse performance in negative tone resists due to higher critical stress before collapse (JVST B 28, C6S6, 2010)

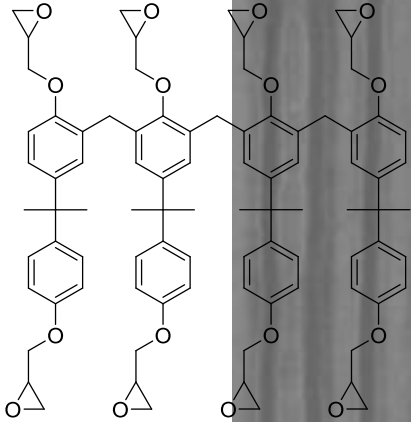


$$\bar{E}_f = 3\bar{E}_s \left(\frac{\lambda_e}{2\pi h_f} \right)^3$$

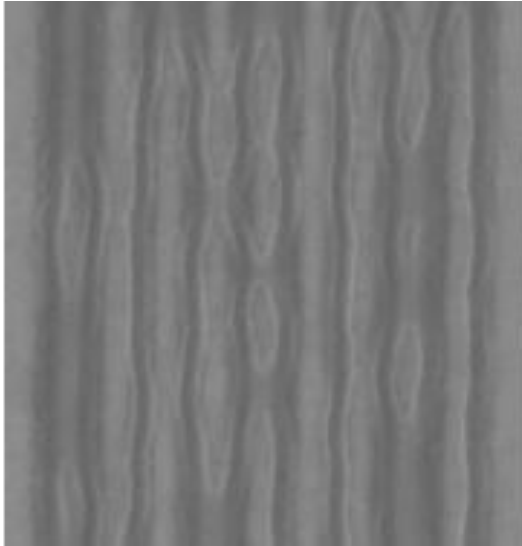
Polymer vs. Molecular Resists – 100 keV E-beam 8

Polymer - SU-8

55 nm 1:2

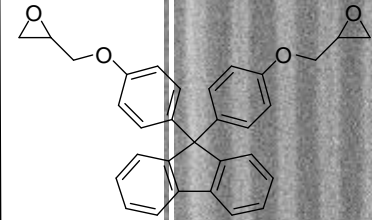


50 nm 1:2

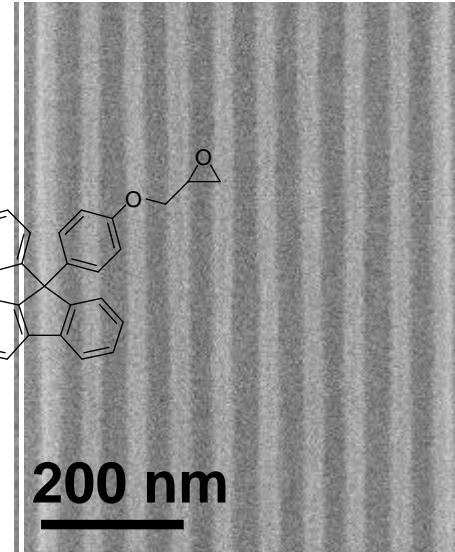


MR – 2-Ep

20 nm 1:2

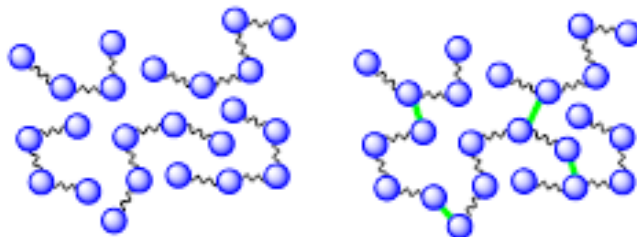


200 nm



- Polymer shows inferior resolution and LER
- Differences likely due to cross-link (XL) density – MR require higher extent of XL to reach full network = better mechanical properties

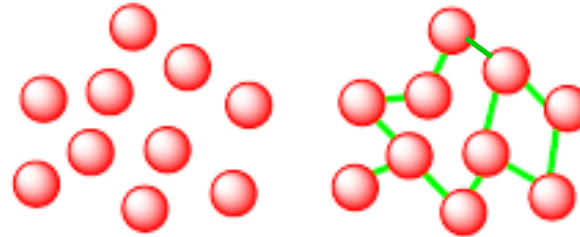
Polymer Resists



Unexposed

Exposed

Molecular Resists



Unexposed

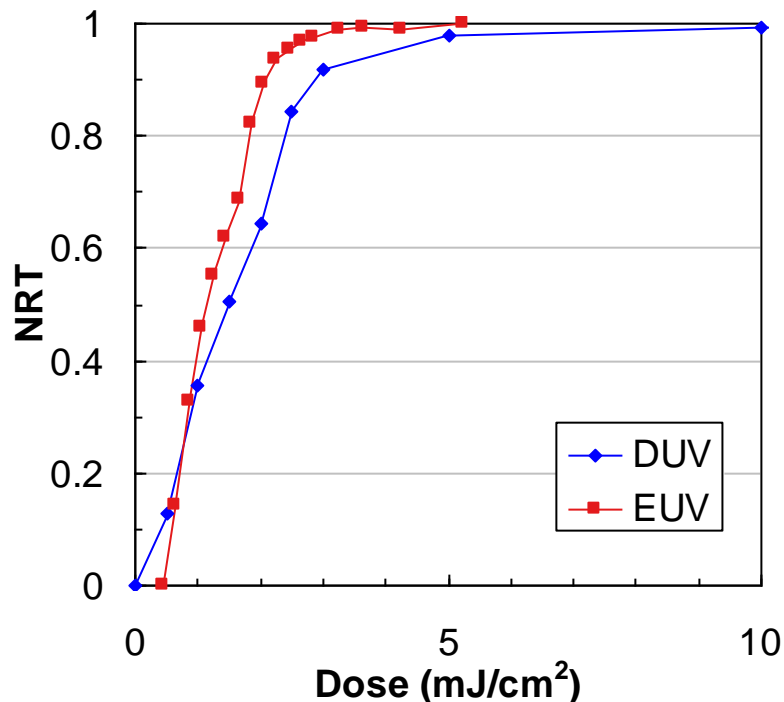
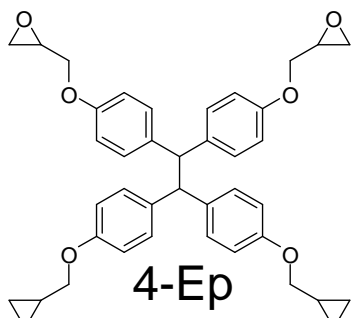
Exposed

E-beam
at
Georgia
Tech on
JEOL
JBX-
9300FS
100 keV

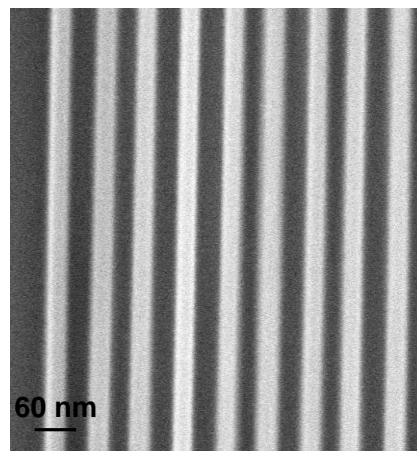


Negative Tone Baseline

- Multiple MR available, but 4-Ep (below) is baseline material for all EUV
- PAG: TPS-SbF₆ 5 mol%, Developed in MIBK (organic solvent)
- Lower contrast reduces performance in EUV compared to e-beam



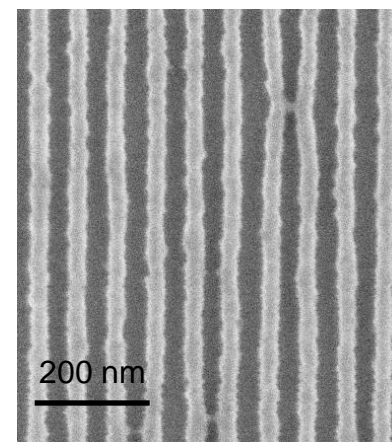
E-beam 100 keV



Esize = 40 $\mu\text{C}/\text{cm}^2$
 CD = 35 nm
 LER = 2.3 nm

*E-beam at Georgia
 Tech on JEOL JBX-
 9300FS 100 keV*

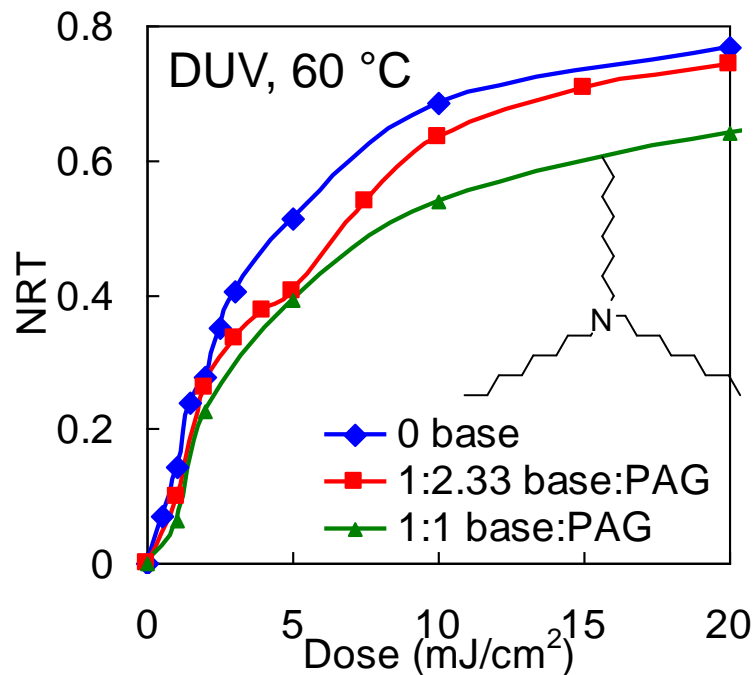
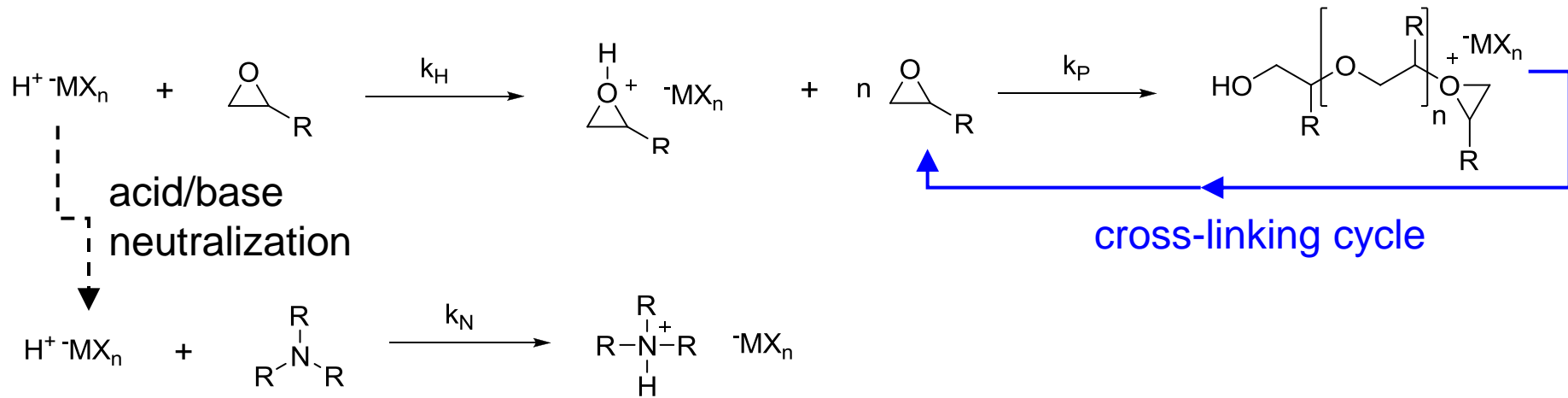
EUV



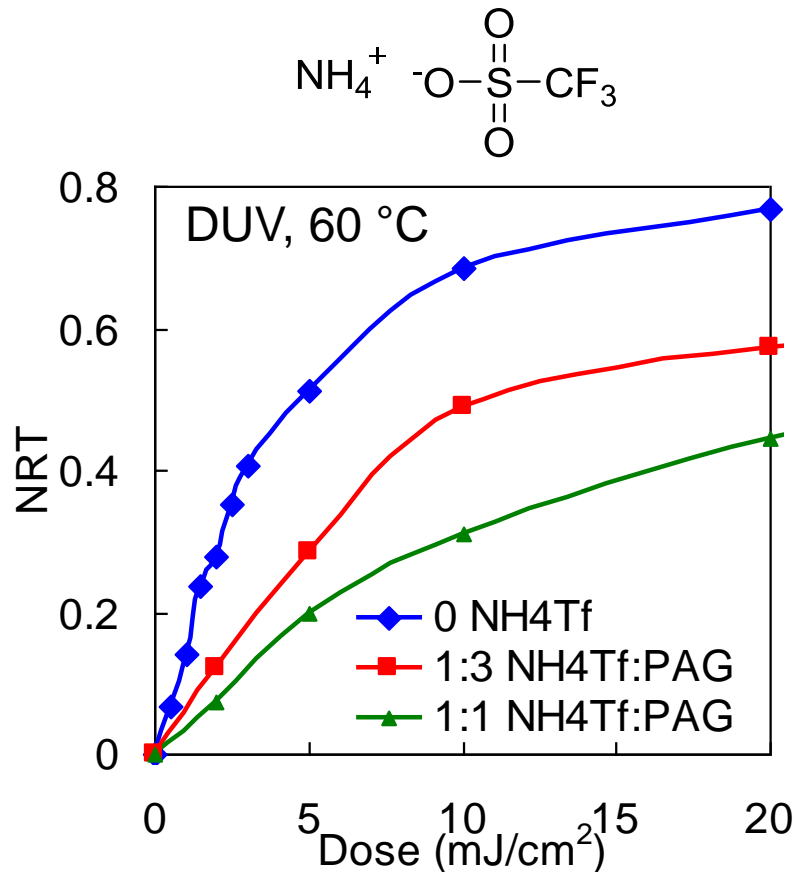
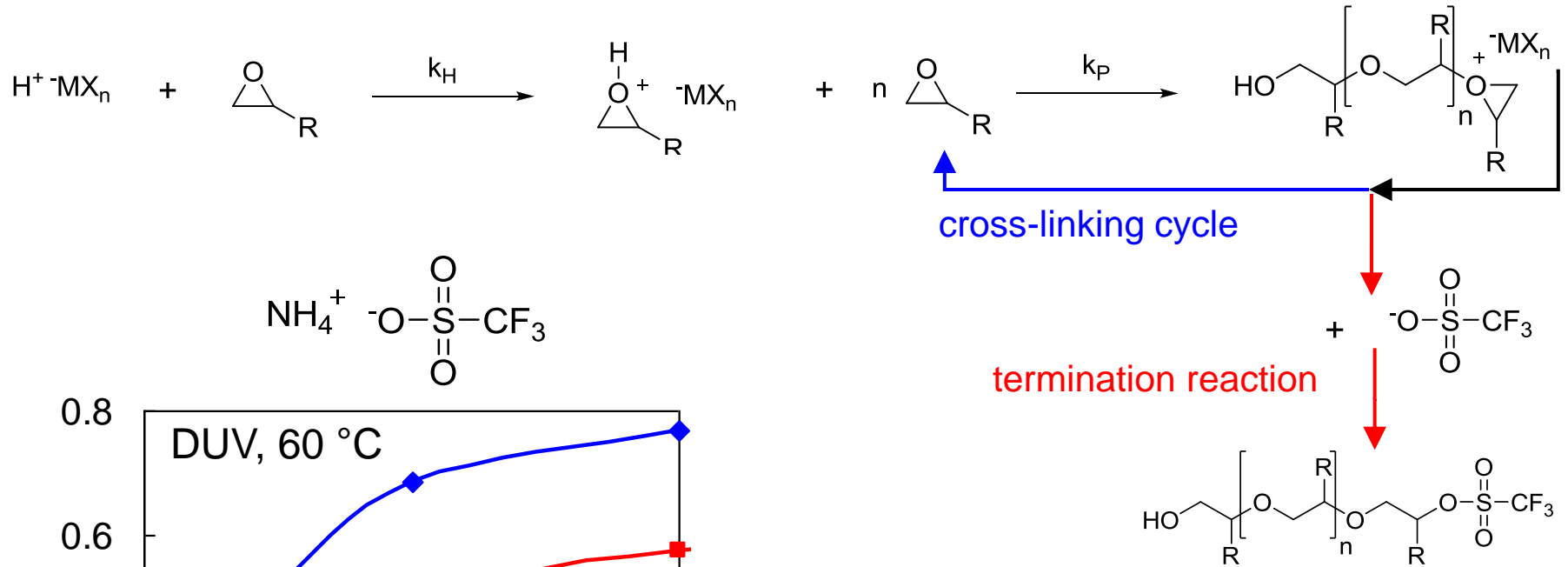
Esize ~ 8 mJ/cm²
 CD = 32 nm
 LER = 4.9 nm

*EUV at Paul Scherrer
 Institute*





- Conventional CARs use base to improve resolution by acid quenching
- Base quencher ineffective in these systems because acid not active species (trioctylamine in 4Ep on left – even equimolar base:PAG ineffective)

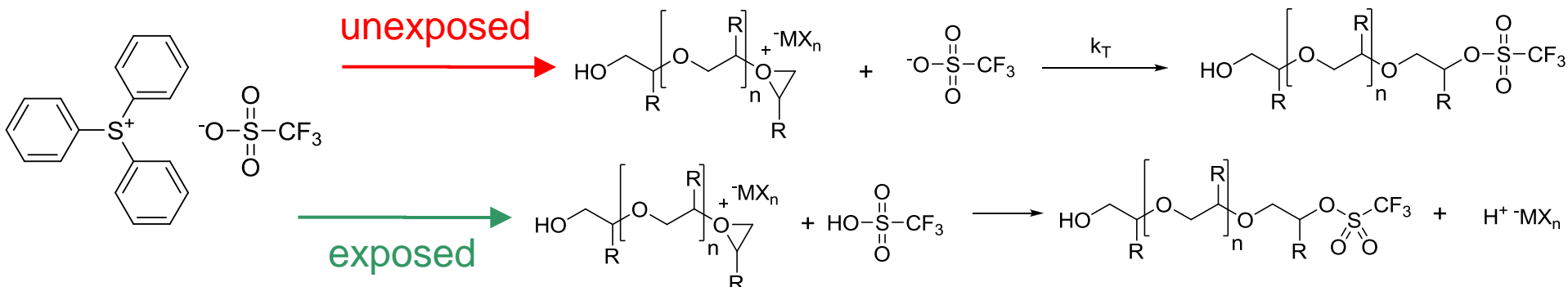


- Cross-linking cycle must be controlled by chain termination or reducing rate of cross-linking reaction
- Triflate anion can nucleophilically attack growing chain to act as chain termination agent and modifies rate of cross-linking
- Addition of ammonium triflate has strong effect on cross-linking (left plot), but we can do even better than this

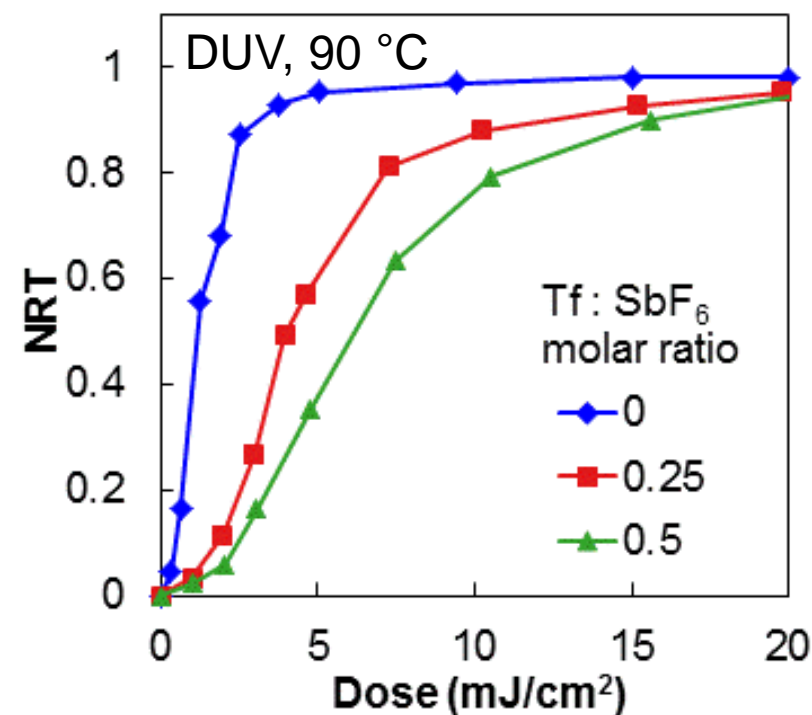


Additive to Control Cationic Cross-Linking

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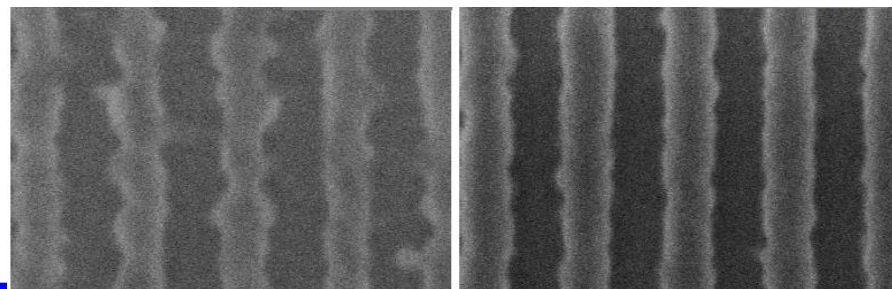


- Addition of TPS-Tf shows chain termination when unexposed, but chain transfer when exposed (photoacid is regenerated)
- By adding TPS-Tf on top of a constant amount of TPS-SbF₆ (PAG at 5 mol%), we see immediate effects on contrast (left plot)
- This causes a shift in the contrast curve to higher dose, but improved performance in terms of LER and resolution

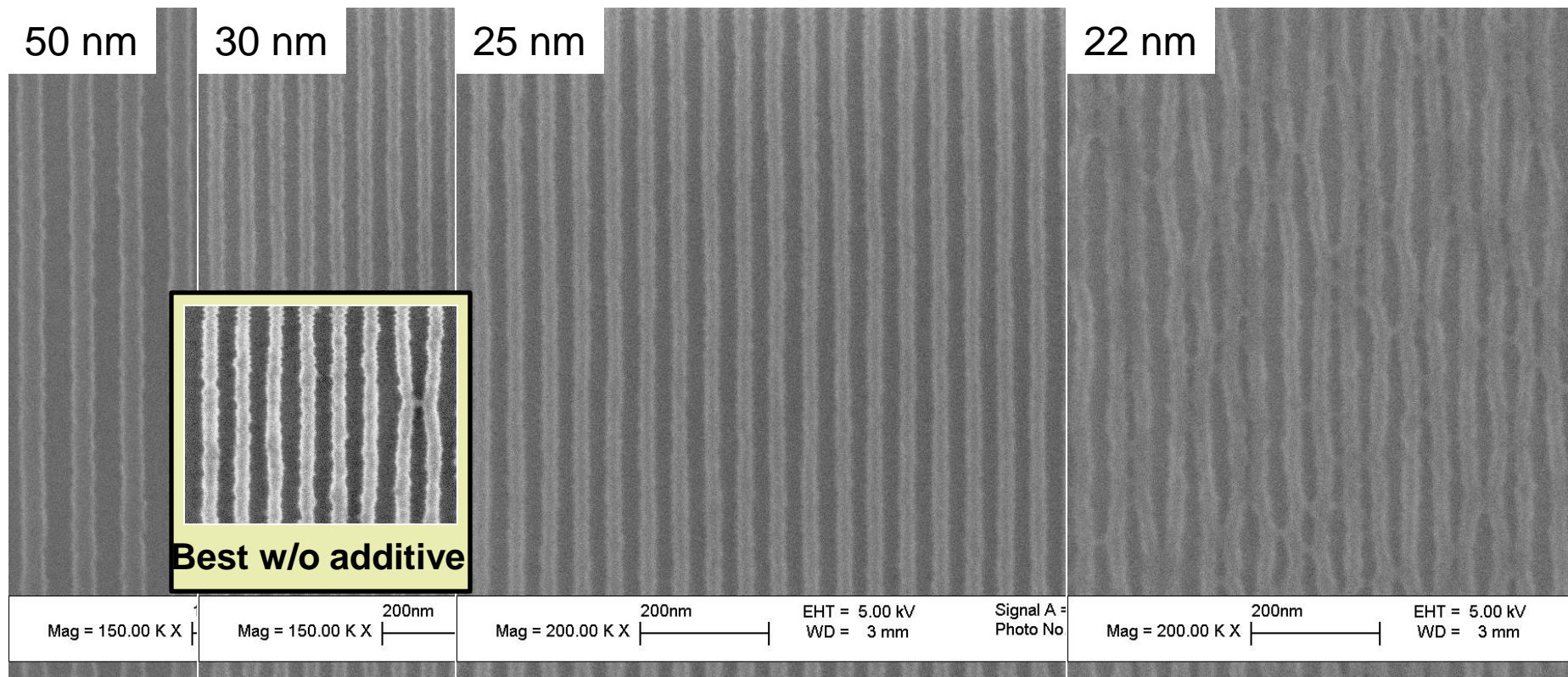


0 additive

0.5:1 add.:PAG



Additive Enhances Performance

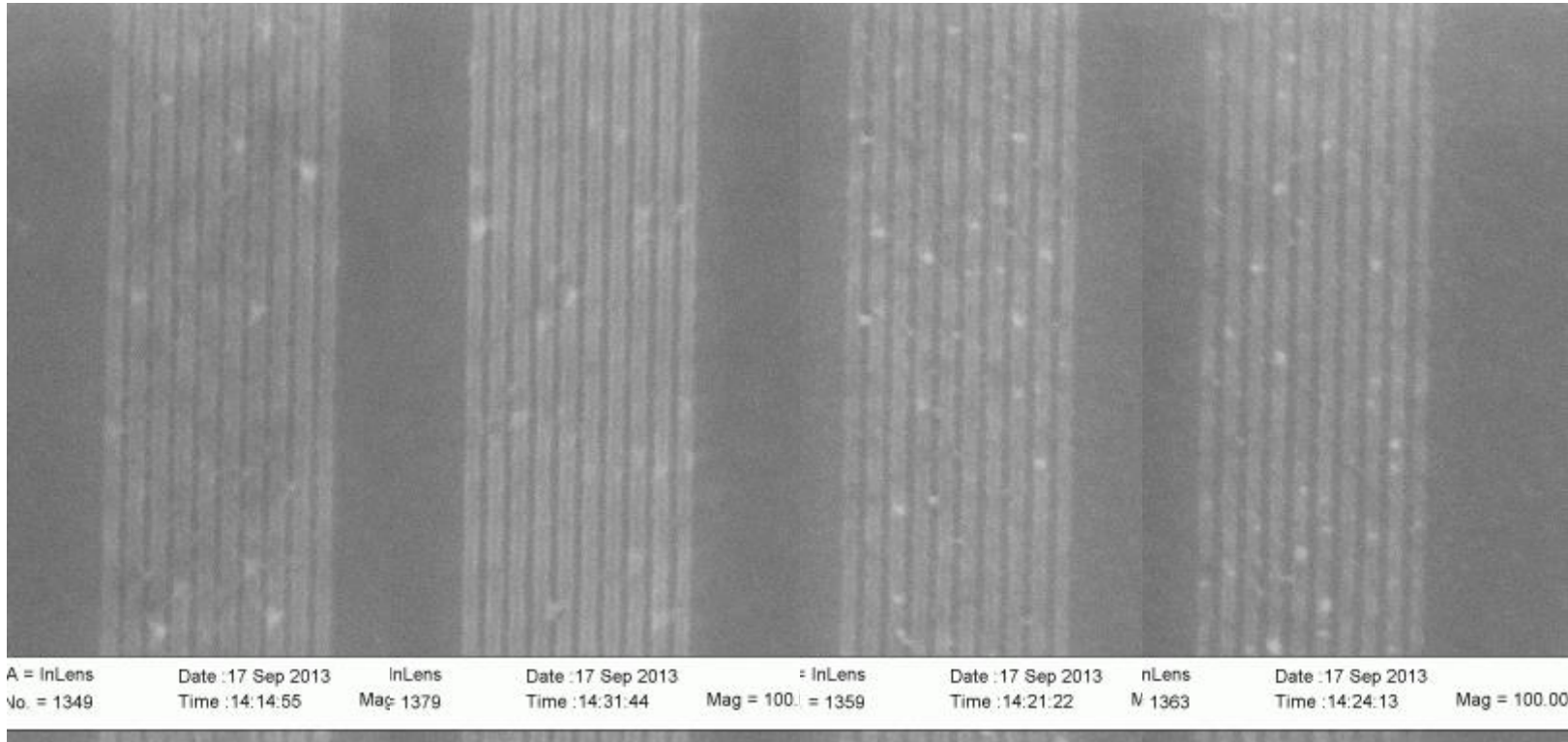


- Significant improvement in resolution and LER – 15 mJ/cm²
- Resist Formulation: 0.5:1 TPS-Tf:TPS-SbF₆
- LER (3 σ) = 4.0 nm for 50 nm lines, 4.5 nm for 25 nm lines
- 22 nm lines resolve, limited by pattern collapse

*EUV at
Paul
Scherrer
Institute*



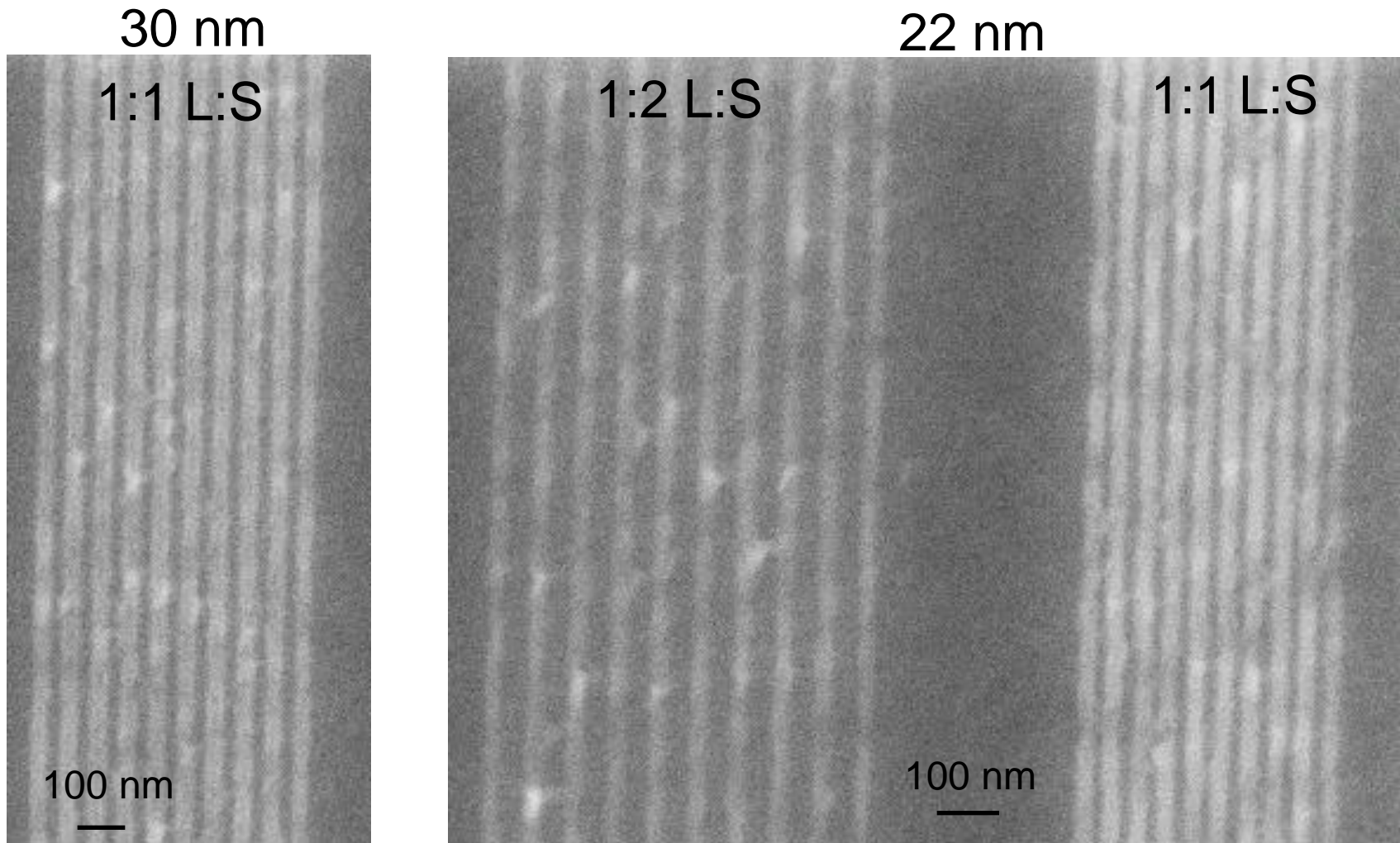
Testing Performance on MET Tool

41.0 mJ/cm²35.8 mJ/cm²31.3 mJ/cm²27.3 mJ/cm²

- New studies carried out on MET tool at Berkeley using dipole illumination with standard dark field mask
- First test was slightly overdosed – minimum dose was 27.3 mJ/cm² for 30 nm 1:1 lines shown above



1:1 and 1:2 L:S Patterns



- 30 nm and 22 nm L:S patterns resolve, but overdosed



Dense 1:1 Line/Space Features

26 nm

22 nm

20 nm

100 nm

100 nm

100 nm

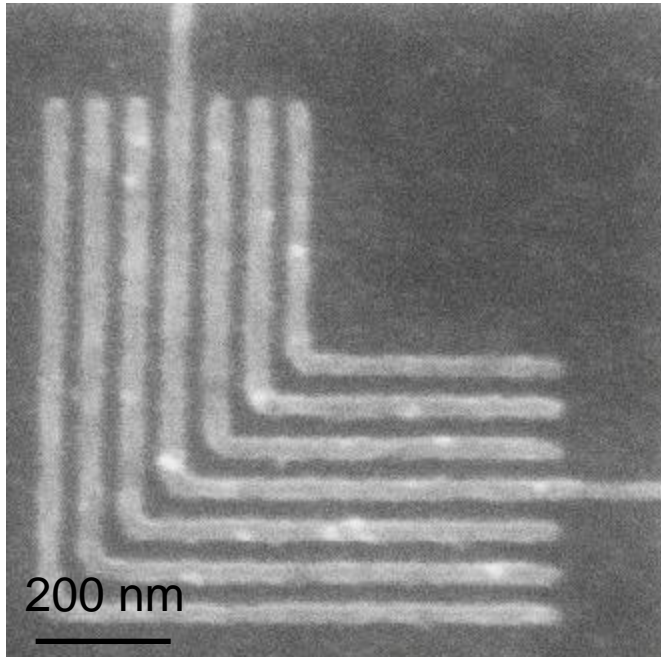
*EUV at
LBNL MET*

- 26 nm patterns on MET look good, but overdosed, a few bridges
- 22 nm and 20 nm dense features resolve, but much more bridging defects and some line bending

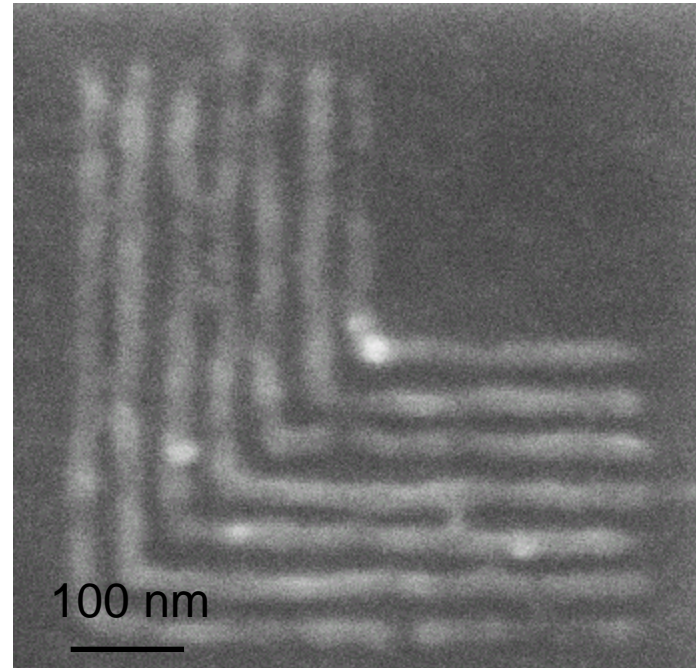


1:1 L:S Elbow Features

30 nm



20 nm



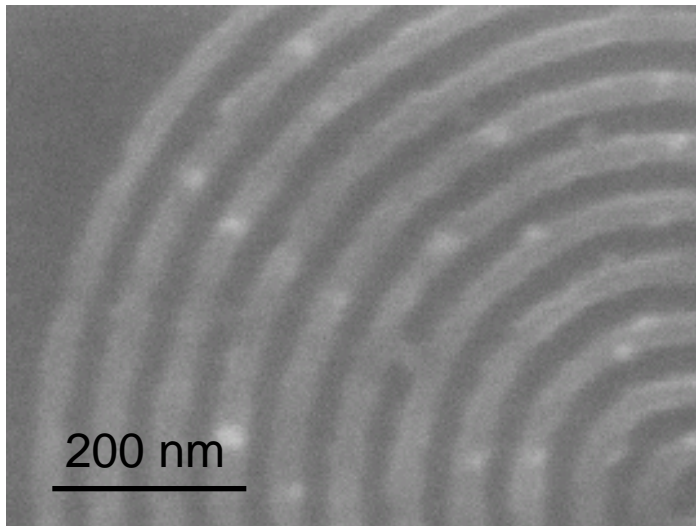
*EUV at
LBNL MET*

- 30 nm dense elbow features look good, but slightly overdosed
- 20 nm elbow features resolve, but some pattern collapse/bridging defects observed

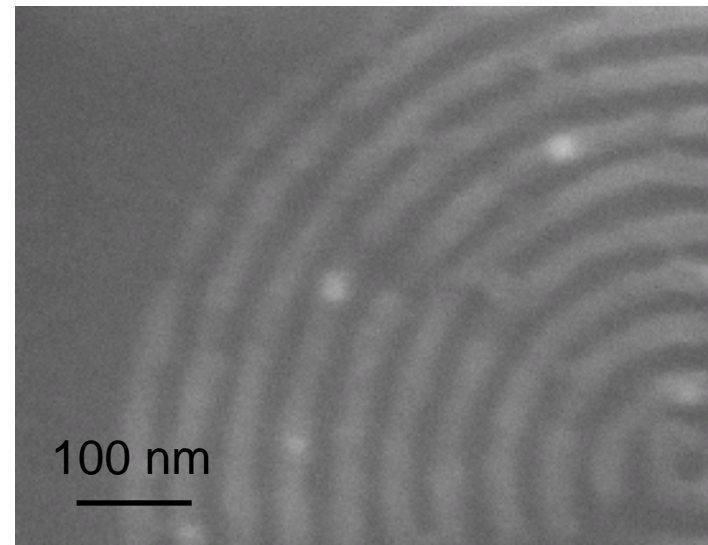


Dense Circle Features

30 nm

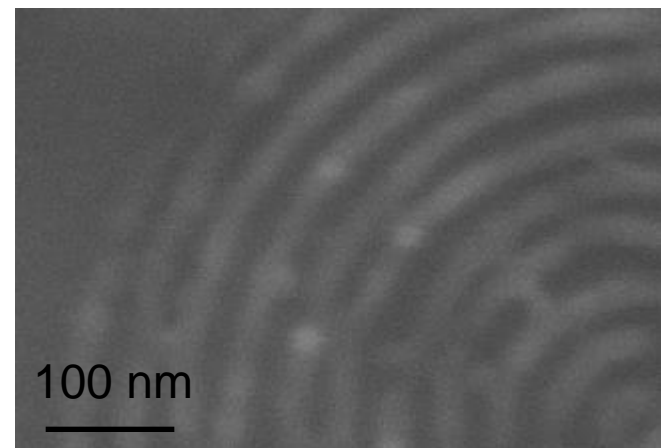


22 nm



- 30 and 22 nm circle features look good with minimal bridging
- 20 nm circle features have more bridging defects, but appear to adequately resolve

20 nm



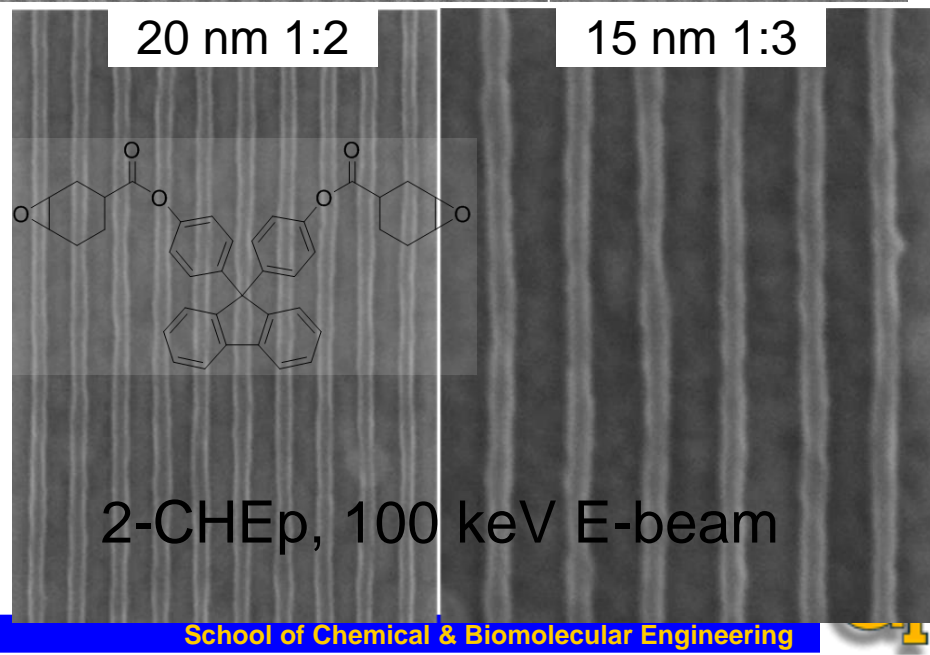
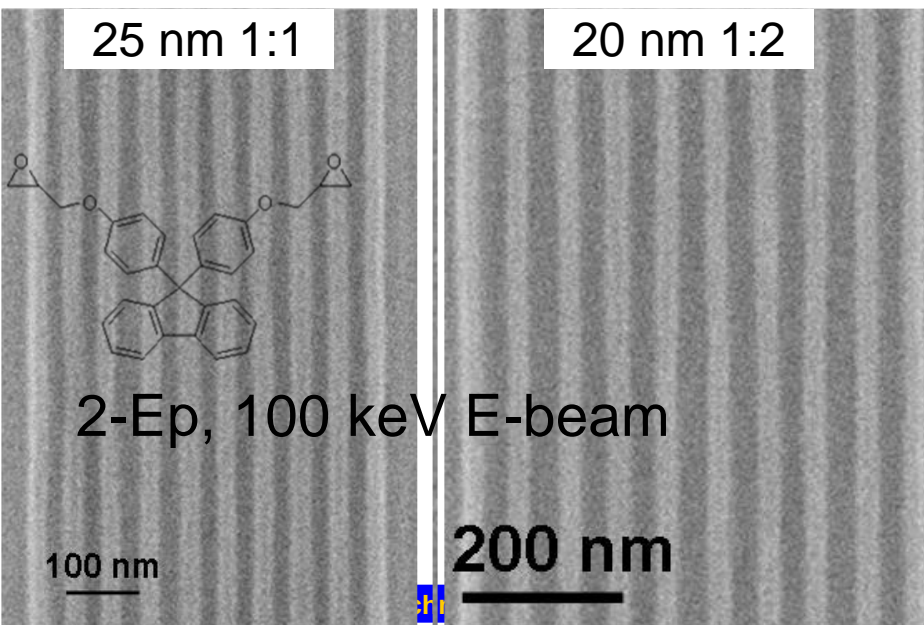
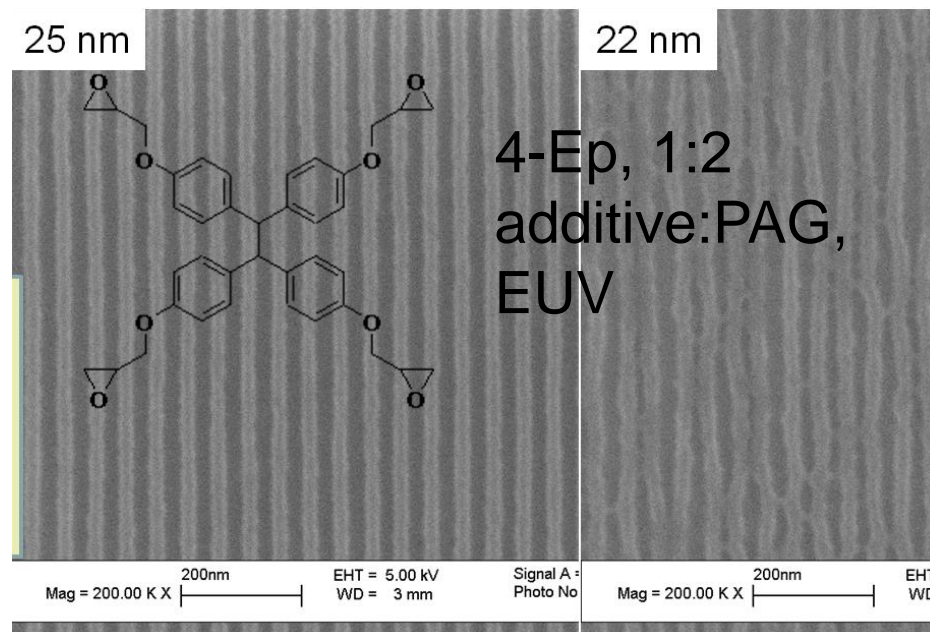
*EUV at
LBNL MET*



Pushing Toward Sub 20 nm Resolution

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- Initial studies on these materials suggest they potentially can obtain sub-20 nm resolution
- Un-optimized 2-CHEp appears to have at least 15 nm intrinsic resolution (resolution limited by x-link reaction)
- The highest resolution materials (2-Ep and 2-CHEp) have not yet been investigated with additive or studied at EUV



Summary

- Negative tone molecular resists based on cross-linking show promise to satisfy EUV patterning requirements for 22 nm and below
- Potential benefits include: superior mechanical strength, intrinsic diffusion control, low outgassing of resist, and reduced swelling vs. polymers
- Controlling of cross-linking/polymerization by addition of novel control additives is key enabler for improving resolution and LER
- Standard illumination conditions on MET shows capability for 20 nm resolution with dose-to-size less than 25 mJ/cm².
- Plenty of room for optimization still exists in already high performing systems

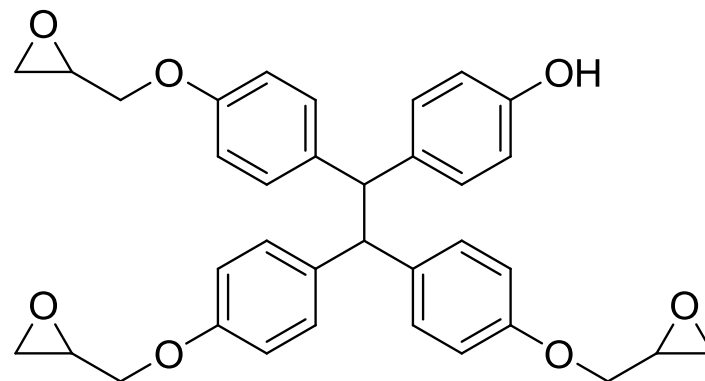
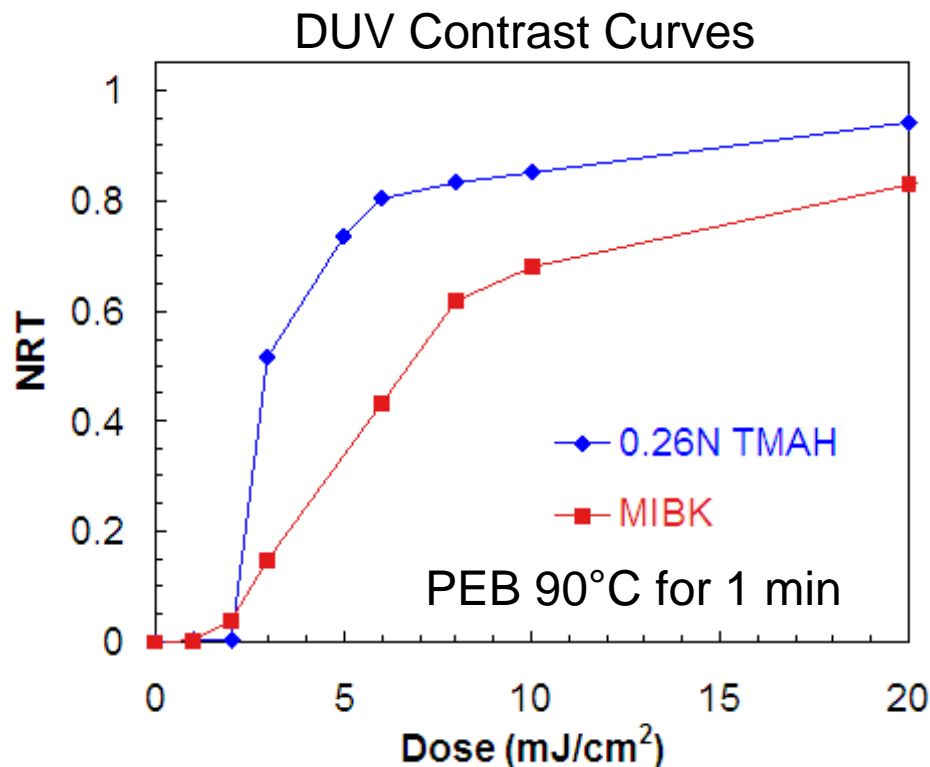


Questions



Additional Slides



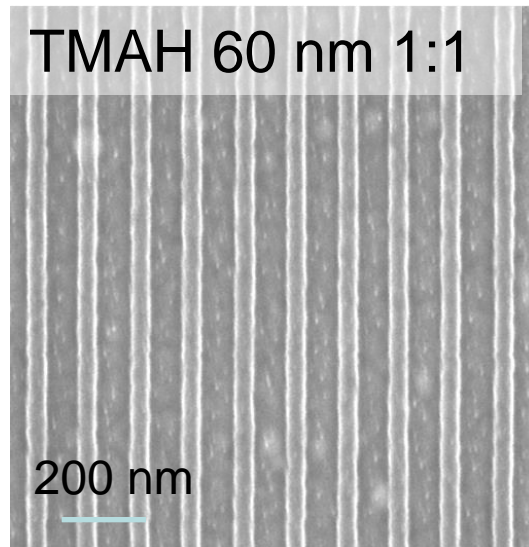
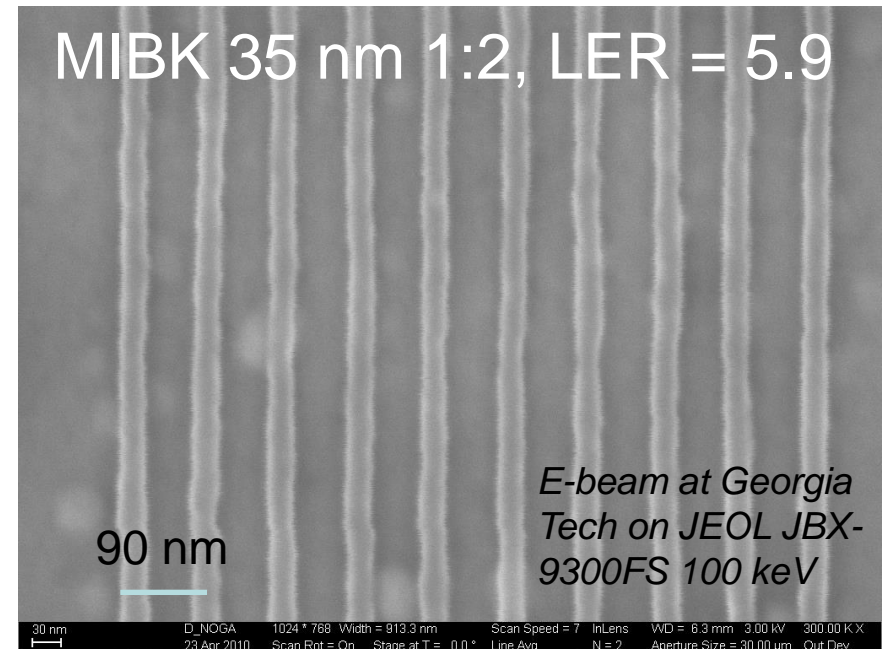
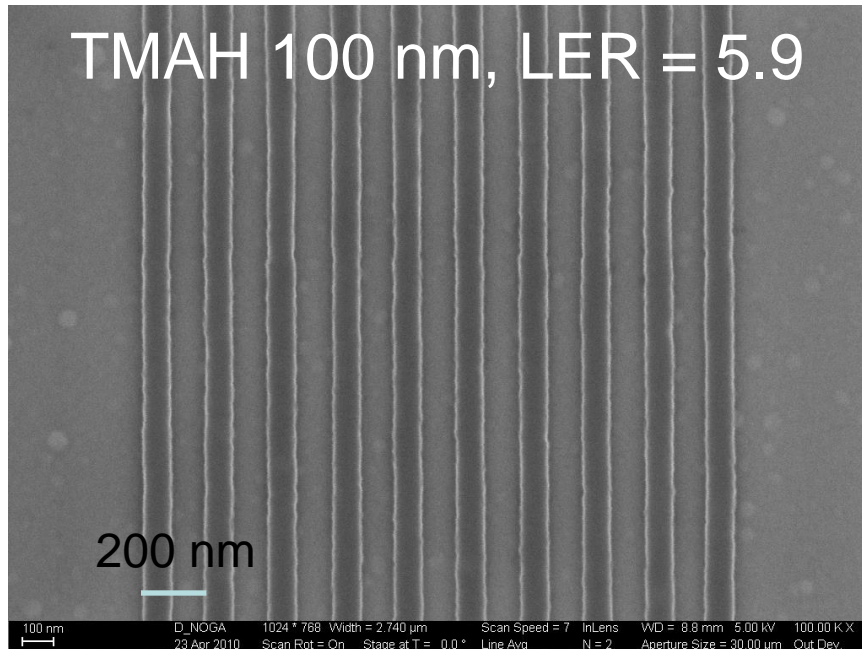


Only 1 OH required for solubility

- Partial functionalization allows aqueous base developed systems
- Unique opportunity for direct comparison of solvent vs. base development
- Shows better contrast than 4-Ep, E_0 shifted away from 0 mJ/cm²,
- No measurable swelling from interferometry studies in solvent or base



TPOE-3Ep 100 keV E-beam Patterns



- MIBK resolution comparable to 4-Ep
- MIBK and TMAH have equivalent LER
- Sensitivity and LER are very similar between organic solvent and aqueous base develop, but resolution is slightly better in solvent

